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PRACTICAL ASPECTS OF CHROME TANNING

REPORT OF A SYMPOSIUM

sponsored by the

DELAWARE VALLEY TANNERS' CLUB
NEW ENGLAND TANNERS' CLUB
TANNERS' PRODUCTION CLUB OF CANADA
TANNERS' PRODUCTION CLUB OF WISCONSIN

at the

Fifty-second Annual Meeting
of the American Leather Chemists Association

Mackinac Island, Michigan
June 20, 1956

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The Leather-making Symposium sponsored by the combined Tanners' Production Clubs of the United States and Canada constituted the concluding session of the Fifty-second Annual Meeting of the A.L.C.A., held at the Grand Hotel, Mackinac Island, Michigan, June 20, 1956. Mr. W. R. Lotz (Albert Trostel and Sons Co.) presided. The panel consisted of Messrs. C. A. Martin (E. Hubschman and Sons, Inc.), N. C. Benrud (S. B. Foot Tanning Co.), Harold Bernard (G. Levor and Co.), J. W. Wolfe (Beardmore and Co., Ltd.), G. F. Shephard (Geo. A. Shephard and Sons), and Jean Rosen (Blanchard Bros. and Lane).

In his opening remarks Chairman Lotz thanked the committees representing the several clubs and called attention to the very welcome presence for the first time of the Tanners' Production Club of Canada among the sponsors.

He reviewed briefly the scope of previous symposia, their origin and purpose, and announced that the present symposium would be restricted to the subject of chrome tanning. He emphasized that the panel members did not propose to make speeches but hoped to introduce ideas and promote discussion from the floor.

The American Leather Chemists Association

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CHAIRMAN LOTZ: To start off the symposium, I suppose the first question that must be legitimately asked is, Why do we chrome tan? I have asked Mr. Martin to start the discussion and present his own ideas on the reason and background for chrome tannage.

MR. CHARLES A. MARTIN (E. Hubschman & Sons, Inc.): This can be answered simply. We chrome tan in order to effect a quick and economical conversion of skin into leather and to impart to the leather the characteristics which we desire. We could go a little further and probably be facetious about it. We chrome tan because that is the way we are set up. We chrome tan because our predecessors have done chrome tanning, and we might even say some people who are chrome tanning are still doing it one way because that is the way their plants are operating, and they may be a little reluctant to push ahead and try something else because everything is going so nicely.

Actually, the purpose of chrome tanning is to impart to the leather the characteristics which have been set up as a standard and which we wish to continue to supply to our customers.

Now, how to do it is a matter for each individual tanner, and that is probably what should come out this morning. I think we ought to try to raise some comments from the floor to start this subject off. If you want to start with calf, that is quite all right.

CHAIRMAN LOTZ: Just to pick up the ball for a second, let's discuss why we chrome tan. What do we get out of a piece of leather that comes from chrome tanning? What does chrome do that other materials do not do? Historically, vegetable tannins were used before the mineral tannages. We found that the vegetable tannages had certain defects. One was the matter of shrink temperature. Under certain heat conditions we found that the leather would not stand up. The first significant advantage that I think most of us got from chrome tannage was an increase in the shrink temperature, particularly in that the leather was able to withstand steam and the steaming and lasting operations which went on in most shoe factories. That to me is the most significant advance brought about by chrome tannage. From the original chrome tannage tanners have gone on to other mineral tannages which give them the same range of shrink temperatures. But historically, chrome did it first, and in addition it is perhaps the most accepted and cheapest material that we have today for tanning.

MR. MARTIN: Yes. I think at this point we ought to have a little discussion from the floor on this chrome tannage. It is the quicker way. It is a more economical way. The big change was, as Mr. Lotz said, the shrink temperature, plus the fact that the tannage could be accomplished within a matter of hours. This applies to a straight chrome tannage. We are not talking about any additives. That will come out later.

MR. H. FRANKLIN BROWN (Robson Leather Co., Ltd.): What is the significance of a high shrink temperature? Why is it important in producing a commercial piece of leather?

CHAIRMAN LOTZ: Some of you fellows who have had to make service calls on shoe companies should know the answer to that. I will answer if no one else will. Let's just say the practical problem we have is getting the upper leather for shoes through some of the lasting operations. In order to do so, many of the lasters are run hot or run with steam, and the leather must stand this particular condition. It is true that manufacturers make a lot of shoes with straight vegetable tannage, but the manufacturers have to baby the vegetable tannage through a shoe factory. With chrome-tanned leather, or chrome and vegetable combination-tanned leather, they do not have to baby the leather in the shoe factory, and the shoe men like these forms of leather for this reason.

I will point out one significant addition to this discussion: You seldom find work-shoe leather that is made by straight vegetable tannage because work shoes are jammed through the shoe factories. They are made inexpensively, and the manufacturer has to have a tannage which stands up to the handling of a general production line. Work shoes or military shoes cannot be handled like little children.

MR. ALFRED G. FLEISCH (Pfister and Vogel Tanning Company): To keep the discussion going, which came first? Did they make shoes because the chrome tannage was added, or the other way around? Or was it because they had chrome-tanned leather that they could make shoes cheaper and speed up the operation?

As far as the wearability of the shoes is concerned, is a high shrink temperature necessary? Perhaps if we did not have leather that would stand a high shrink temperature, shoes might be made differently. I don't know. I just raise the question.

MR. PETER R. BUECHLER (Tanners Research Corporation of New Jersey): I think some discussion on the part of the panel as to the effect of the pH of the stock prior to chrome tannage, the amount of chrome put in, the pH to which you neutralize, and the effects of these things on leather properties,

would be something I would like to hear. It is an easy question to ask, but I am sure the answers will vary.

CHAIRMAN LOTZ: While your panel would like to get into the technique of chrome tanning as quickly as possible, may we just hold that off for a second? We have talked a little about the history of chrome tanning. I think a necessary introduction, before we go on to talk about pH, might come from ourselves and from the technical men representing the chrome companies and suppliers—that is, thoughts about the actual manufacture of chrome liquors. It seems to be a logical sequence to talk first about the chrome tanning materials and chrome liquors, and go from there into the technique of chrome tannage.

MR. HAROLD BERNARD (G. Levor & Company): I take it we are still on the subject of the shrink test in connection with chrome tanning. That is where we started. Now, I think you had some explanation, and I think you jumped from the tannery to the shoe factory. But it seems to me the shrink test, first, is a guide for the tanner in regard to how well the tannage has taken hold of the leather. I think it indicates whether you have reached the optimum point of tannage. Further, I think that the shrink test is very important when you put the leather through the other operations. For instance, drying—if you dry by hanging the skin up, or even by pasting, the yield will suffer if you do not attain the proper shrink test in tanning with chrome. Would somebody like to add something to that?

CHAIRMAN LOTZ: Since there is no comment, we will go on from the shrink temperature to a discussion of the manufacture of chrome liquors. There has been a considerable difference of opinion on the manufacture of chrome liquors. Let's just look over the situation as it exists. Some tanneries reduce their own chrome; some tanneries buy prepared prereduced chromes; some tanneries use a two-bath process; some use a one-bath process.

Among those that use a one-bath process and reduce their own chrome some add the sugar last in preparing a sugar-reduced liquor; some add the acid or sulfur dioxide last. I wonder if we could not get from the people who handle prepared chromes or bichromate of soda some thoughts on the actual reduction. Is there anyone who might want to talk about the actual reduction of chrome liquors?

MR. N. C. BENRUD (S. B. Foot Tanning Company): The old standby process is to take the bichromate, add the acid, and then run in the sugar. What you are trying to do is to get and hold as large an amount of volatile organic compounds as possible. I believe most tannners have found that this type liquor will produce a better and fuller leather.

Generally, you will find that most tanners try to maintain certain temperatures during the reduction process to maintain uniformity. There are some who

have gone to the extent of adding a means of refluxing so that they keep the volatile organic compounds in the liquor. A great deal of work has been done and published on determining these organic constituents. If somebody here has done some recent work and would like to talk about it, we would be happy to listen to him.

CHAIRMAN LOTZ: Do we have anyone who would like to comment on the preparation of chrome liquors?

MR. BROWN: If we use molasses in place of glucose, we can save $6,000 a year. Is there any good reason why we cannot use molasses? Are there likely to be ill effects arising from it?

CHAIRMAN LOTZ: Has anybody had experience with molasses in sugar-reduced liquors?

MR. FLEISCH: During the well known sugar shortage some years back we used some molasses and could not tell the difference between the leathers. If the liquors were made with the same basicity, there was very little difference between them.

MR. BROWN: Thank you. I wonder how many people use molasses, and if not, since there is a substantial saving involved, why don't they?

CHAIRMAN LOTZ: That is a good question. Among the tanners present, suppose we have a show of hands on people who use molasses. It would be indicative to the industry if we knew. Is there anybody here using molasses?

MR. R. SELVARANGAN (Central Leather Research Institute, Madras, India): In India, for the manufacture of chrome-tanned uppers, the leather industry used molasses and sawdust in making their chrome liquors. With sawdust-reduced chrome liquors they are getting good results. The only thing is that the liquor will be somewhat brownish because the molasses contains iron and calcium, but there is no discoloration of the leather, and the leather is good. They prefer the organic-reduced liquors to inorganic-reduced liquors.

CHAIRMAN LOTZ: Apparently molasses is not yet a commercially accepted material here.

DR. LUDWIG SELIGSBERGER (Quartermaster Research and Development Center): I believe that the main reason is that molasses foams very much, and the reduction of the liquors takes much time and is very costly because of labor, whereas corn sugar-reduced liquors can be made in a very short time—maybe in an hour or two. To reduce with molasses would take four or five hours.

CHAIRMAN LOTZ: Adam Lammert asked me a question the other day having to do with the use of sulfuric acid. Apparently in New England there is a question of not using commercial 66° Baumé sulfuric acid, but something with a lower Baumé.

MR. ADAM M. LAMMERT (Chemtan Company): In New England we are using 58° Baumé acid, and there is some question whether it is better to use a stronger acid and have a much better action, and more thorough action, on the grain of the side. But this problem has not really been investigated, and I don't believe that any solution has been found. So far it is only a private investigation.

CHAIRMAN LOTZ: You indicated a private investigation. Is this a generally accepted thing in New England?

MR. LAMMERT: No. It is only what would be called a hunch of a few working constantly with both high and low Baumé acids.

CHAIRMAN LOTZ: Why does it become a problem? Is it due to the fact that a 66° Baumé acid is not as readily available?

MR. LAMMERT: I could not answer that question. It is probably only a question of economics. It is much cheaper to buy 58° acid than 66°, but there are great difficulties in storage connected with the use of 58° Baumé acid.

CHAIRMAN LOTZ: And those difficulties would be mainly corrosion?

MR. LAMMERT: That is true. There is another thing. Most of the tanneries have a bate, pickle, and tan process, and during the short time of pickling they would like to have the pickle acid go through the grain layer as fast as possible to take care of all the stains that come into the sides or skins during conserving and storing them. We have a large number of iron stains, and all these iron stains originate in that New England way of sulfiding and liming—we have tanneries with a 24-hour liming process, and large amounts of sulfides are being used. A strong pickle must be used to take care of the stains, otherwise we would not eliminate the stains, and we would have blue stock which is not suitable for light pastel shades or whites.

MR. ROLF QUARCK (Chemtan Company): Why would it be any problem to use a 58° acid as long as the volume of water is kept constant? If it is just a matter of less concentration, you could use a little less water, couldn't you?

MR. LAMMERT: This may be so. I have no information on that question.

MR. BEN A. GROTA, JR. (Fred Reuping Leather Company): We had a certain amount of experience during the time that 66° acid was short. We had

available a source of 60° sulfuric acid which we used. We had a couple of tank cars of it at least, and we used it in our pickling and in our chrome reduction. It was our experience when making allowances for quantity of acid, that we had no trouble with the reduction or boiling, and we could see no significant difference in the resultant leathers.

CHAIRMAN LOTZ: Any other experience with lower degree Baumé acids?

MR. SELVARANGAN: When we used the organic materials for reduction, we used to have difficulties when we used concentrated sulfuric acid. In preparing a sawdust, we put it in hot water, and then all the sawdust is added, and we have had no difficulty with our reductions and no external indications.

MR. BENRUD: There is one problem that would come in when using a different Baumé acid, particularly if you are living in the north country. The freezing point of sulfuric acid is very critical, and it is necessary to hold it within a very close tolerance or it will sludge out in the winter.

MR. C. ALLEN LAUDER (Wickett and Craig, Ltd.): Isn't this just a matter of purity? If it were just a matter of concentration, if it concerned a lesser concentration as was mentioned before, you would use less water because the 58° sulfuric acid would contain more water. But I would think this is a matter of purity—of how pure the 58° Baumé acid is compared with the 66°.

CHAIRMAN LOTZ: Apparently then, the use of 58° Baumé acid is not an unusual thing. In other words, there are quite a few tanners who have found some economic advantage in using this particular acid, because it is less expensive than the 66° Baumé acid. I suppose we are all good enough chemists so that we can get over the problem between 58° and 66° Baumé.

Now, to go on to bichromate. Bichromate is usually sold in two forms. One is liquid and the other is a crystalline material. Bichromate would be the third material used in the reduction. Are there any who have experienced differences in their chrome liquor between crystalline material and liquid material? Have you had any experience in your tanneries to indicate to you that they have run into a problem with a liquid versus a crystalline material?

Just as a matter of interest, let us poll the people who reduce their own liquors to see how many tanneries represented here use liquid bichromate. Six or seven. How many use crystalline? Six or seven. It seems to be pretty evenly divided, and it is probably mostly a matter of storage and handling rather than the materials themselves.

Now we come to the actual reductions. Mr. Martin, do you want to comment on that?

MR. MARTIN: Actually we do not reduce or make our own chrome liquor. It is our opinion that the suppliers, the people who make these tan liquors, are in a much better position to give a more consistent and uniform product than you are yourselves, with due respect to all the efforts you may put into it. We feel that the tan liquors that we buy are more consistent, and the uniformity of our leather reflects it. There are enough problems in a tannery at the present time without going into all the problems of making tan liquor, and we feel that the manufactured tans are far superior to those that we would make ourselves. We have worked both ways, and that is our conclusion. There are other things that influence us—storage and space. However, the leather itself is much more uniform from the tan that we buy. So it is our stand that if you want to make chrome liquor, that is up to you, but we feel that the tans made by the companies that specialize in that are the better tans to use.

MR. DAVID R. SMALL (Brezner Tanning Corporation): We have lightly passed over a couple of the crucial and debatable subjects, I think, on the making of liquor. I refer to the possible variations in reduction technique that can be employed: concentration, higher or lower reaction temperatures, sequence of additions, rate of additions, etc. What are the relationships between these variations in reduction technique and the ultimate leather properties derived from tanning with liquors produced one way or another when other conditions are held constant? What are the advantages or disadvantages in leather properties to be attained from keeping more or keeping less of the volatile organic reaction by-products, as these differing procedures necessarily will do? I would like to hear that expanded on.

MR. BENRUD: I believe more volatile acids are produced if you do the reduction at 100°C. than at a lower temperature. Also, a smaller amount of oxalates will be formed. This applies to a closed system where sugar is added to the acid bichromate solution. Very few tanners care to have oxalates in the chrome liquor. There is also quite a difference in the concentration at which different people do their reduction; however, most tanners end up with a liquor containing 12 to 15% chromic oxide.

CHAIRMAN LOTZ: I might ask Mr. Small to discuss this further.

MR. SMALL: The reason I brought it up is that there is no set rule, there is no single formula, for going about chrome reduction. I was interested in hearing some comments about the relationship between actual leather produced by a chrome liquor made in one fashion and that made in one of many possible varied fashions. What are the practical results of varying the actual reduction procedure?

I believe we agree that the procedure can be varied in an almost infinite number of ways. What I am trying to find out is what the reasons are that caused any one of the group to end up with a particular combination.

We have one combination. We wonder if ours is the ultimate, or should it be varied further to try to improve on it by a different approach. Rates of additions? Concentration? Sequence of additions and temperatures, and so forth? I am not trying to solve any specific problem. It is just the general principles behind chrome liquor preparation, and the relationship between these principles and our end products, that we are trying to get at here.

MR. THEODORE D. BRAUNSCHWEIG (Loewengart Tanning Co.): I have some experience in making different types of chrome liquors, and generally speaking, I would say this: that the sequence, putting acid in first and following with the glucose or other organic reducing agent, or putting the sugar in together with the chrome and following with the acid, makes two fundamentally different liquors. For a pre-tan I personally prefer to mix the organic reducing agent with the bichromate and add the sulfuric acid, because it produces a higher amount of masked chrome compounds which act for a finer grain and a more evenly tanned stock for the chrome leather.

But adding the acid second requires a higher amount of acid, because the usual amount of acid would be insufficient to complete the reduction. On the other hand, for a chrome liquor with a higher basicity, used after the initial chrome tanning has taken place, it is not necessary to have a higher amount of masked chrome. To summarize, mixing bichromate and glucose, followed by acid, gives more oxalic acid and more compounds masked with oxalates, and the mixing of bichcromate with the acid, followed by the glucose, gives less masked chrome.

MR. GUY CREESE (Creese and Cook Company): It seems to me we are begging the question here. Procter stated that the presence of aldehydes and ketones was a very important factor in the preparation, and that retention of these compounds and esters in the preparation of one-bath chrome liquor was important.

Now they have come along to the use of sulfur dioxide gas in the reduction. I have never thought that you produced the same result with SO_2 as with an organic reducing agent such as glucose or molasses. Other people think you do. Also, in the preparation of the sulfur dioxide liquor they have introduced certain organic agents to try to duplicate what you get with the organic reducing agent.

I don't know whether anybody has done research on that. Perhaps Dr. Turley could tell us. But it does seem to me that over the years there has been a lot of shadow-boxing in regard to that feature.

We were reducing our own chrome liquor, but the man who was doing it reached retirement age. When we tried to get a younger man to do the work, we had trouble with the union which contended that during the process of reduction gases attack the membrane of the nose. So we have gone over to the prepared tan. But I have never thought that we exactly duplicated what we

did by reducing our own liquor with an organic reducing agent. I would like to hear that debated, because it seems to me that in this day and age we should know whether those esters and ketones and aldehydes are doing work there or whether they are not.

CHAIRMAN LOTZ: A challenge was thrown at you a moment ago, Dr. Turley, to let us know your views on this subject.

DR. H. G. TURLEY (Rohm & Haas Company): It is, of course, only an accident that for chrome tanning the tanner starts with an oxidized material, bichromate. That goes back to the beginning of chrome tanning. If we had started with just a chromic oxide dissolved in acid, things would have been simplified.

Virtually, the tanner, when he started making chrome liquors from bichromate, became a small chemical manufacturer. Naturally, there were various ways of reducing the bichromate to the trivalent form of chromium. The old literature is full of every kind of reducing agent—sawdust, flour, old skins, or anything you like as long as it is capable of being oxidized and in turn capable of reducing the chrome.

So in the course of time there would naturally be different tanning effects from the different chrome liquors prepared in different ways. And early in the literature there were statements made that the liquors reduced by sugar seemed to possess some special virtues.

We have all heard a lot about masking agents and the by-products of sugar reduction. I won't go into the angle of how you should do the reduction, but if we were doing it in chemical manufacture, trying to do an efficient job of reducing all of the chrome, we would certainly see that all the organic material, in this case the sugar, was burned up and nothing left over. Then we would not have impurities to worry about.

I think when you really examine the question—I know we did years ago—of the amount of by-products of sugar reduction, you would find very little present. Certainly all the volatile materials have gone in drying down, but you may have left a little organic matter; however, from my observation, it does seem to me that the industry has progressed in this sense: that instead of all this talk about the value of the by-products, aldehydes, esters, ketones (which, as far as I know, have never been identified) we have come to have, certainly in the United States, an appreciation of the desirability of taking the simple basic chromium material and then adding to it, by design, organic acids to give certain effects.

I am sure that in that way the chrome tanning industry is making progress. I am sure there is no chrome tanner in this room who, as a reduction expert of bichromate, with organic materials is going to guarantee all the time the absolute formation and control of all the possible by-products. He is certainly better off in seeing to it, either by purchasing or making it himself, that there

are no essential by-products, and if he wishes, adding inorganic acids or other materials to give him the results he requires.

DR. SELIGSBERGER: Dr. Turley is right insofar as the volatile by-products, among which are aldehydes or ketones, cannot be present to any extent. But it is true that the amount of by-products depends on the excess sugar. We can rest assured that the chrome extract industry does not use more of its reduction material than is absolutely necessary.

The tanner, on the other hand, who makes the chrome liquor himself, sometimes uses vast excesses. The minimum amount required is below 30% of the weight of bichromate used. During the war many tanners may have gone down in the amounts of corn sugar used. It is in the low range that the chrome liquors obtained are closest to the commercial tanning extracts. A tanner successfully using a chrome liquor prepared with 50% sugar on the weight of bichromate has an entirely different liquor. It is the amount of sugar which is the key to the reduction.

MR. BRAUNSCHWEIG: I had, in one particular tannery, a personal experience in using different homemade chrome liquors. One of them was SO_2-reduced, and the other was glucose-reduced. I can assure you that the difference in the leather was definitely visible. We used the SO_2-reduced chrome liquor for the pre-tan of patent leather, while on other leathers we used a glucose-reduced liquor. There was a considerable excess of glucose in the liquor.

Recently I believe Künzel has worked on the SO_2-reduced liquor and found that by using SO_2 as a gas, you end with a 33% basic liquor and that this will always produce a flat piece of leather, which in the case of the patent leathers is rather desirable.

But it is possible to do SO_2 reduction without using the gas, by using sodium sulfite, which increases the basicity. With a higher basicity it has been found that SO_2-reduced liquor can produce the same fullness in chrome leather that would be obtained with any other reducing agent.

CHAIRMAN LOTZ: Have you had an opportunity to use any masking agents with the SO_2-reduced liquor—formates or materials like that—in your comparisons with sugar-reduced liquor?

MR. BRAUNSCHWEIG: In certain cases we did. I have used sulfite chrome, formate chrome, and oxalate chrome, and combinations of sulfite and oxalate chrome, and the differences are visible in the structure of the grain.

CHAIRMAN LOTZ: Despite the masking effect of the additions?

MR. BRAUNSCHWEIG: I would rather say *on account of* the masking agents. The oxalate chrome always gives a very fine and smooth grain. For that reason

I prefer an oxalate-masked chrome for the start of the chrome tanning process. But it is not so desirable if you want to make a leather with a grain which breaks easily like elk. Then oxalate chrome would not be so desirable because you get such a tight grain that you have difficulties in graining it.

MR. QUARCK: Isn't that a rather sweeping statement to make, that you get these different results with oxalate or sulfite or formate? Isn't it largely influenced by the quantities used? In other words, in the case of oxalates we know that if we use too much, we get a very poor tanning effect, which in itself would make for a smooth grain. With acetate, if we go above a certain molar proportion, we detan. So it is more a matter of taking any one masking agent and working it out for your own conditions.

What Dr. Turley brings out is that by working it out in your own tannery, for your own particular use, you are in a position to get a far more uniform product by starting with a 33% basic liquor, which contains no by-products, and then adding whatever you want to add, if anything.

MR. BRAUNSCHWEIG: My statement refers only to the first stages of the tanning. In these tests one-third of the total chrome used was used in pre-tanning. To complete the tanning, a glucose liquor of 45 or 48 basicity was used.

MR. BENRUD: Did you say a high basic SO_2-reduced liquor, before?

CHAIRMAN LOTZ: I think I caught the same thing. You said you used in these tests, or were able to produce, a high basic SO_2-reduced liquor?

MR. BRAUNSCHWEIG: No. I was only quoting Dr. Künzel, who worked on it and published a paper recently. By increasing the basicity the fullness of the chrome tannage obtained was identical to that obtained with any organic-reduced liquor—by using the sulfite as reducing agent and increasing the basicity right from the start.

MR. LAUDER: We are starting to hear quite a lot about basicity in chrome liquors. What is the optimum basicity? We are hearing 33%. It seems to me that 33 is being used in a lot of tanneries. Is there an optimum? Or why are a lot of tanneries using 33% basicity chrome liquor?

DR. TURLEY: Might I ask this question of Mr. Lauder and the rest: Having used the 33% basic liquor, what basicity actually have you, considering the pickle in this case, that case, and other cases? At what basicity are you *really* tanning? It is what the Lehigh group call the over-all basicity.

I think it would be better if we steered in that direction, because whether the chrome liquor is 33 basicity or some other figure, this is only one side of

the story—whether you have a highly acid pickled skin or a low acid, and so on. We should be thinking in that direction, I believe.

CHAIRMAN LOTZ: I see Mr. Chain sitting back there. He has been doing a lot of work with chrome for a long time. What is your experience with this over-all basicity versus so-called high basicity versus medium basicity?

MR. J. THOMAS CHAIN (Diamond Alkali Company): The story of basicity from my experience is like Dr. Turley's. If you stick to a pickle pH of 1.5 and put 33% basicity liquor on top of it, your system is probably 20% basic, and if you pickle at 2.8 and put 33% liquor in there, your over-all basicity is about 30. The basicity thus depends on the amount of acid in the pickle. It is the over-all story that ultimately determines the basicity and not just the basicity of the tan liquor. It is the basicity of the tan liquor, minus the pickle acid.

MR. QUARCK: One question on that point: Suppose you start in one case with a more acid skin and use a more basic liquor, and in another case with a less acid skin and less basic liquor— would you expect about the same result?

MR. CHAIN: That is a question. I don't see why you would not get the same result. It is still the average basicity of the two products that counts—the pickle and the tan. The minute you drop the tan down, the thing should average out.

MR. ANDREW SALAMATOV (Barrett and Company, Inc.): I do not think that I can agree with that statement. The tanning depends upon penetration. Penetration depends on particle size. If you start with the high-basicity liquor, you have large particles, and if you add acid to it right away, it does not change the particle size as quickly as you think. Now, on the other hand, if you have a low-basicity liquor, the particle size is smaller, and therefore penetration is more rapid, and the result cannot be the same.

MR. SMALL: How about holding some of these factors constant and discussing the results obtained when varying the others? Suppose we start with a given pickle and discuss the results of varying the basicities that are used on top of that given pickle, which will then eliminate the question of the over-all basicity because the over-all basicity will then change according to the basicity of the chrome liquor if we start with a given pickle concentration.

CHAIRMAN LOTZ: I think it is time for a tanner to put his foot in this door and make comments. Isn't what we are talking about here mainly the philosophies of our tanneries themselves, and the type of leather we are trying to make? For example, we have a tannery that manufactures mainly heavier types of leather where the smoothness of the grain is not so important. In a tannery such as ours we are more interested in high-basicity liquors because we do not care so much about the grain.

If we had to compete today with fine kip producers like Armour Leather, Rueping, or Beggs and Cobb, and with the type of smooth lightweight kip dress leathers they make, we would have to change our chrome tanning system entirely. We would have to go to lower-basicity liquors. We would have to go to more acid-type pickles and endeavor to keep the grain as flat and tight as we possibly could, to compete in that type of business.

We can argue the basicity forever, but I think it is mainly a question of what we are trying to produce. I would say that perhaps organizations like Pfister and Vogel, ourselves, the Northwestern Leather Company, and S. B. Foot, exist in one separate business world, the side leather world. And organizations which work 40-pound hides and 35-pound hides have another set of problems, because they are aiming at other types of leather. And someone else who is running 25-pound hides, or oversize kips, has a separate kind of business.

To clarify this discussion we almost have to define the type of leather we want to produce when we are talking about basicity.

In our tannery we have one of the thickest lime streaks as far as pickling is concerned. We have an extremely high pH, acid-wise, coming out of pickle. We use a 42-basicity liquor and our over-all basicity, as Dr. Theis used to calculate it, was extremely high.

The end result of this tannage, plus a high-pH beamhouse, is that we get an extremely plump piece of leather, with a not particularly smooth grain. But for our type of business, where we make stuffed retan leather, where the leather is highbacked or whitened, or where we are doing a lot of buffing, the size of that grain is not so important.

Suppose for a few minutes we go to the opposite end, an end that I know so little about, and that is the making of lightweight smooth dress leather. I can only prognosticate that they would use a very acid pickle, and that they would use a low-basicity chrome, probably masked with an oxalate to keep the grain as flat as possible. In tanneries that use that sort of approach it would be quite difficult to make a boarded or grained leather because the grain would be too tight and the tannery would have cracking problems at the staking machines.

I introduce these ideas because I wish to be argued with. Mr. Chain, you started this. Will you argue with me about it?

MR. CHAIN: You are right. If I were going to make calfskin or kips, I would start with a low-pH pickle and a low-basicity tan. With the type of side leather you make, your system balances when you put the chrome on. You don't have as much acid, and you use a high basic chrome liquor, so that I believe your basicity drops very little as a result of adding the chrome.

CHAIRMAN LOTZ: Have you any ideas of what pH you would recommend for various types of leather? Suppose you are making small kips, at what pH

would you bring your leather out of the tannage? Who is making small kips dress-size, or calfskins, and would like to express an opinion on that? There must be others here besides Mr. Martin. Is Mr. Waite here, from Gallun?

MR. P. H. WAITE (A. F. Gallun & Sons Corporation): I don't know that I can create much of an argument here. From my experience, which is rather limited from an over-all standpoint, in general we are inclined to stay close to the acid side, at a pH around 3. We have done a little work with formate leathers at a considerably higher pH, which seems to give fairly good results, I would say, from a grain standpoint.

Our leather is somewhat different from that of almost everybody else in the business, so that it is a little hard for me to compare them. After all, we do use syntan in our tannage, and that in itself has quite an effect on the grain surface.

I would like to hear from somebody else who is more used to working with a straight chrome leather.

MR. MARTIN: Mr. Chain made a statement before about starting with a low-pH pickle and using, I think he said, a relatively low basicity liquor.

MR. CHAIN: Yes.

MR. MARTIN: By a low basicity you mean around 33?

MR. CHAIN: Yes.

MR. WAITE: We operate at a fairly high basicity ourselves, and we cannot see that the basicity of the chrome liquor, in itself, is too important a factor. It seems to us that the pickle has more effect on the final result, as far as basicity is concerned. Too, I think it makes a difference how you add the liquor, and when you add it, and so forth. But actually, I am inclined to believe that the pickle itself has more effect.

MR. MARTIN: I will go along with you there. I would agree with a lower-pH pickle and then a low-basicity tan. But Mr. Salamatov, you start at a little higher pH. As I remember from last year, you said your pH is considerably higher than I would consider proper. That, of course, is your setup. Everybody here is going to change it. In fact, the amount of acid you are going to use in your pickle may be determined by the streak that you are bringing in from the lime. But the whole thing has to be balanced out in the end. So you cannot say that the optimum is a low-pH pickle and a low-basicity tan. You may mask and you may not. But I know your problem is different because you start with a much higher pH in your pickle. Your over-all basicity may be the same, but you obtain a different piece of leather than the others do.

MR. SALAMATOV: Let us first reach an understanding when we talk about pH. Are we talking about pH of the leather or the liquor? I assume it is pH of the liquor that we are discussing right now.

MR. MARTIN: I would believe that is it.

MR. SALAMATOV: As far as the pH of the liquor is concerned, I would not say that it matters very much, because it is a component of many different factors, as has been said already. The problem is, how you want to end your tannage—at what pH you want to get your leather. That is the important thing, rather than the pH of the bath at any given time.

I think the discussion has been confined mostly to the pH of the liquor, and I do not believe we can arrive at any real understanding of any problems if we talk about the pH of the liquor itself because there are any number of factors which will enter into the pH of the skin—the streak, the basicity of the chrome liquor, the different additives, whether salt or formate, or anything of the sort. They all change the pH of the liquid to some extent, and so do the time of running, and rate of running, and temperature.

They all, in one way or another, will influence the composition of your liquid—its hydrolysis—and with the hydrolysis the pH will change constantly. So I do not know if there is any such thing as an optimum pH as far as the pH of the chrome bath is concerned.

As far as pH of the leather is concerned, I think, as it has been said by Mr. Lotz, that it depends on what you want to make. We prefer to have a very fine grain, and therefore we adjust our liquid in such a way that we do have the fine grain. The pH of the skin we try to keep in the neighborhood of 3.5.

CHAIRMAN LOTZ: Suppose you raised the pH to, let us say, 4? We know your grain might change slightly. Would the temper of your leather also change? As a tanner you might be less interested in the grain characteristic of a certain type of leather and more interested in the temper or some other characteristic in the leather. As tanners, Mr. Salamatov, we are interested in a number of things in our leather. Suppose you vary your process a little bit, what else is changed besides the grain?

MR. SALAMATOV: Grain and the over-all result are what you are after. We never go by one single factor. The leather is examined from several points of view. And when it is examined on the table, nobody ever looks into the pH alone.

I don't quite understand just what you are driving at. We started with pH, and now you want to go into something else. Maybe we should finish with pH somehow, if we can.

CHAIRMAN LOTZ: What I am trying to obtain, and what I am hoping I can hear from you, is an expression of opinion on pH versus various characteristics of the leather. I inferred from what you said that you are, in your particular operation, primarily interested in the grain of the leather.

MR. SALAMATOV: Yes.

CHAIRMAN LOTZ: Because of the type of leather that you make?

MR. SALAMATOV: That is right.

CHAIRMAN LOTZ: Would it be possible that someone else in the same type of business would be more interested in characteristics of the leather other than the grain?

MR. SALAMATOV: Certainly. I think they might.

CHAIRMAN LOTZ: Suppose you became interested in other characteristics, would you vary the acidity of various parts of your process or stay with the same basic process?

MR. SALAMATOV: Well, the answer to this would depend on how much of a departure there would be from our regular way of doing the tanning. If we wanted to get something considerably different, probably we would make some adjustments. But if the difference would not be very significant, we would make adjustments somewhere else.

MR. BERNARD: I would like to comment on the topic so far. Many years ago we made our chrome one-bath liquor from day to day in barrels, and we made one day an excellent piece of leather and another day a poor piece of leather, so that the boss commented along the lines of Mr. Martin's idea: "Please give me Campbell's soup; add water and use." Ever since that time this has worked out in all but special tannages.

To get back to pH, the subject is a very interesting one. I believe control of the pH is the most important factor in chrome tanning. Whether the leather is going to be retanned has a bearing on what pH we arrive at.

Further, I believe that the old system consisted mainly of using a low-basicity chrome and starting to feed bicarbonate or borax or some other salt about halfway through the tannage to raise the pH in order that the skin would stand the desired heat test.

Today I believe it is practice with the many different types of bought chrome tanning agent to buy one with the pH which works best for your process. In some cases it is advisable to start with a low pH for half of the amount of the chrome and then finish with a high basicity, either for certain types of smooth,

tight, full-grain leathers or, as Mr. Lotz mentioned, the full, rougher-grained leather which tans very quickly and is going to be more of an elk-type leather.

I would like to hear the comment of anybody here who has had the experience of neutralizing partly with a high-basicity chrome rather than using the old system of bicarbonate and such.

MR. BRAUNSCHWEIG: I believe it would be well to make a statement here which so far has not come up in the discussion at all. It concerns the basic facts of chrome tannage as such. One of the factors which is of the utmost importance has not been discussed at all, and that is concentration.

The golden rule for tanning requires starting the tannage with chrome compounds of small-particle size and ending with a large-particle size; this holds more true for chrome tannage than for anything else. In observing this we have to look at the chrome tannage from this point of view: The chrome in liquors of high concentration has small-particle size, just the opposite from the vegetable tannage. Therefore, basicity ties in with the concentration. You recall, for instance, the dry tannage of Schorlemmer, which is operated with less than 50% float altogether and where the chrome is added in one shot. By this process you obtain a nice full piece of chrome leather, and yet the basicity of the liquor can be as high as 48 to 50%. But the concentration of the liquor is so high that the chrome, when it goes into the leather, is of the smallest-particle size. As it falls on the fiber the concentration is reduced, the basicity also is reduced, and you obtain a fully acceptable chrome tannage.

Therefore, the thing is this: that the whole chrome tannage—pickle, chrome tannage, and neutralizing—is a very finely organized system which, in each individual tannery, is handled according to a specific process, and this produces the type of leather which this particular tannery is aiming at. Therefore, it is not possible to say that this basicity is good for the start and that basicity is good for the end. You have to consider all the factors through the pickle, from the start of the tannage to the end, and each individual factor has a definite specific meaning for that particular tannage. The argument of the preference of a low basicity or high basicity has to take into consideration all the other factors which are involved in the tanning process.

And here we come to the point just brought up about the neutralizing. If you start out with a fairly moderate pickle and a low basicity in the beginning of the tannage and end up with a high basic chrome, you can forego, most probably, the neutralizing completely, which will improve your grain.

But if your acidity in the whole system is so high that the chrome is not set properly, then you have to resort to the addition of alkali in order to obtain the point of tannage which you want for your particular type of leather. And it is not necessarily true that you have to obtain a high shrinkage test. Sometimes the chrome leather has different and more desirable characteristics if you do not bring it up to a fully neutralized point with a high shrinkage temperature.

MR. BROWN: Our pH is 2.5 before the addition of soda, and 3.5 when we pull the leather out. How does that fit in with the general picture?

MR. SALAMATOV: Is there any such thing as a general picture?

MR. LAUDER: I am not going to answer Mr. Brown's question. I am going to answer Mr. Lotz's question, which I think was very important, and which I am afraid we have passed by. It has something to do also with Mr. Brown's question, that is, the question of pH.

Mr. Lotz asked the question, if the pH were raised above 3.4 to 4, would it affect the temper? Now it has been found in our tannery that if the pH is raised from 3.5 to 4, and possibly a little above that by neutralization, it does affect the temper. We get a more flexible leather, and we find we get a little more stretch.

DR. TURLEY: I would like to go back to Mr. Lotz's question of a moment ago. I think it is one of the most important things, and we could not give enough time to it, certainly not today. That is the question of the grain pattern.

That, gentlemen, is one of the outstanding characteristics of leather which is always going to differentiate it from plastics. I know that plastics can be embossed in certain ways. I realize that. But they still do not have the characteristics of leather. So this question of the grain pattern is most important.

Now it so happens that chrome tanning is really an art, in spite of all the scientific explanations we have tried to bring forth, and the way it is manipulated makes it an art because of the tremendous possibilities that are inherent in running one and the same basic—I mean by that, fundamental—tannage.

Could I be permitted to make a sketch on the board?

CHAIRMAN LOTZ: By all means.

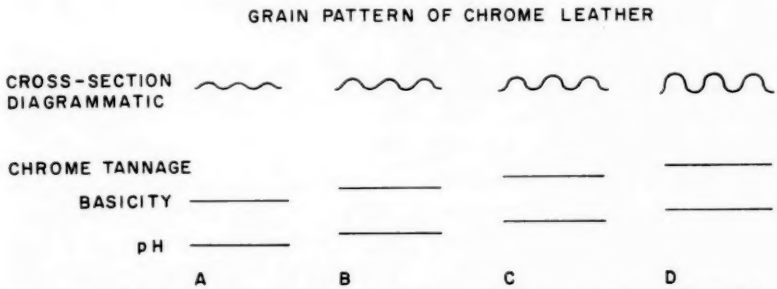

FIGURE 1—*Relation between grain pattern of chrome leather and basicity and pH value in chrome tanning.*

DR. TURLEY: Now, gentlemen, with one and the same skin you can manipulate it in such a way that you wind up with these grain patterns (Figure 1). The shoe people here are unkind: They have not mentioned the glove people, and who makes smoother leather than the fine glove tanners?

Here we have the fineness of grain, which is a feature of glove and garment leather, *A*. Then you have a fine-grain soft shoe leather here, *B*. An then smooth, light side leather here, *C*, that is not so fine of grain. And finally here you have a heavy side leather, *D*, which is usually corrected on the grain.

These leathers seem to be related in some way. This first type of leather, *A*, is made more with the acid type of tannage—more acid in the pickle, with low-basicity chrome, and so on, all the way up the scale. If you want to relate it to pH, the pH is gradually rising like this, and very often the chrome content. And the basicity of the chrome goes in the same direction.

This general picture, of course, is all subject to modification; but I know if you study this carefully (and I have done it for quite a few years) that the grain pattern itself teaches you a lot about how the leather was tanned.

I just wanted to bring this out because I feel (and I don't think too many of you disagree) that the grain pattern is one of the very important attributes of leathers and is influenced by the chrome tannage.

CHAIRMAN LOTZ: We make so many types of leather in our tannery that we probably have to expect types of grain all the way from some garment leather, which we now make up in this classification (low or flat grain), to a high grain for mechanical leathers. The general result is that we have three beamhouse and seven chrome tanning processes, all depending on the type of leather that we wish to make. I would say that predominantly we are in the middle range (medium height of grain) due to the nature of our business. Occasionally we must bring through a certain amount of blue stock, which should be in a medium-grain classification but, due to our soaking and other processes, ends up with a pronounced grain. We have a high pH. We have a formate process, drum bate, pickle and tan, and high grain. We get a high grain in the blue and try to move it back to a medium grain by a retannage process, or perhaps an overchroming.

I can tell you this much: It is our experience that once you have set this pattern down at the end of tannage (high grain), there is little you can do by rechroming to move it back to a medium grain. If you have a tannery where you can make a middle type, you can adjust it to go to this end.

Our tannery is at a disadvantage because we cannot substantially modify the grain by a retannage. I hope that gives you a picture of the way we exist as far as chrome tannage is concerned.

The only difference that I might have with Dr. Turley on his pattern is this: I think most of his lines are correct except that perhaps some of the calf tanners might want to change the curve of the chrome line or the amount of chrome.

Particularly in Europe we find that the amount of chrome in calfskins is considerably higher than it is here in the United States, mainly because they wish to produce a flat-grained pattern.

MR. QUARCK: I would like to ask a question about the grain pattern business. Suppose you have your leather tanned and shaved, and now you want to finish the operation prior to the fatliquoring by neutralizing. In one tannery you have very soft water with no hardness at all; so you add a certain amount of alkali, say 0.5% of bicarbonate of soda, and bring it up to a certain point. In another case you have hard water, and you just wash the leather and bring it up to the same point.

I would like to know how much difference it makes, and I think there are very few tanners who can answer that, because in any one tannery you have either one or the other condition. I don't think anybody really knows. But I do think that in the Middle West, generally, the pH's are in a higher range than they are in the East. It depends on what you do afterward, and what the pH should be is something that everybody has to decide in his own tannery. What effect it has on the grain, I don't know either.

MR. LAMMERT: I could not answer this question but I have an additional one: What will longer storage of the chrome-tanned leather do? That means storage after the leather comes out of the tan liquor and is piled on the platform. Will that make the leather smoother? Will we have a higher analysis of chrome later on? Will we have a higher grain? Will we have a better structure which later on will give us a rounder feel in the leather and keep the flanks filled up?

We have to assume that the reaction of the tannage has not been completed after about two or three hours in bicarb. We also have to assume that next morning the reaction is not completed and that the leather has not come completely to an equilibrium. I have indications that in other countries they are attaching a great deal of importance to storage of the leather after taking it out of the tan drum, before setting out, splitting, or shaving.

MR. MARTIN: You have a lot of variables there. I think that the whole thing has to be controlled on almost a straight line. What you do before, and what you do after, are all going to influence this.

We tan to a certain point, and everything that is tanned on Monday will be set out and shaved on Tuesday, and colored and dried on Wednesday. We do not let anything sit around. But I think if you do let it sit around, or rest a day, or age a day, that it will affect your leather from the standpoint that you may have a fuller tan, or it might be a little rounder.

I think you can get into other difficulties, besides, because the moisture content is going to vary because of drying out and you will have difficulties in dyeing. We prefer to have our leather adjusted to a point so that we can

take it right from there and move it as quickly as possible and get it in the dryer and away. There is very little time wasted at that point.

I know there are others who, after the leather is tanned, may let it set. Some do it on horses and some on platforms. There is always a feeling that there is more tan being fixed on draining down. The condition of the skins when they come out of the drum has an effect. We prefer to run the leather straight through. There are others who, for various reasons, do it differently. It depends basically on the setup in your plant—what you have done before and what you will do after. Everything influences it.

MR. JIRUSKA (Davis Leather Co.): We leave the leather on the horse for 24 hours, and the next day we shave it and get it out of the way. But we found out that if we have to leave some of it for a couple of weeks in cold storage on account of holidays, we get a softer, looser leather.

MR. FRED KLIMPL (R. Neumann and Company): We have a similar problem. We find we have a bottleneck in our drying department and that it reflects back to the chrome tanning. Many times we are forced to keep out blue stock for periods of weeks, up to two or three weeks. We found the same results as the gentleman from Davis. The leather was rounder, but much looser.

MR. GROTA: Last year we had a great deal of stock between tanning and wringing. Some of the stock was there 4 or 5 weeks before it was wrung out. We had to make drastic fatliquor adjustments in order to keep the temper within the range which we desired. In some cases we used as little as half or two-thirds of the fatliquor that we would have normally used on that stock, had it been run all the way through immediately. It may have made slightly looser leather on the average, but the big difference that we noticed was in the temper.

MR. LAMMERT: Was the temper better or worse?

MR. GROTA: It was softer than our normal production, so it required much less oil to keep it somewhere near what we considered normal.

MR. LAMMERT: When using less oil, did you get a weaker tensile strength, then, as judged by the ordinary tests of making a cut and trying to tear it out?

MR. GROTA: I cannot answer that. I do not know.

MR. KLIMPL: Did you notice any difference in the chemical reaction?

MR. GROTA: No.

MR. LAMMERT: That question originated through the fact that in the East, where we usually work with very fast processes, invariably the leather that we

color on Monday has a better feel and looks better, and the quality falls down toward the end of the week. We would like to have it stored the same as we would have to, to bridge a holiday of three days, but we cannot afford it and do not have room. So we have to use the same method Mr. Jiruska gave, of taking the leather out, piling it up for 24 hours, and then proceeding with setting out, splitting, and shaving.

CHAIRMAN LOTZ: Since we have been using formates in connection with our own chrome tannage process, we find less of a variation on long periods of drying out than when we did not use formates. We find a greater ease of wet-back and particularly better consistency of coloring. That does not mean that we can store chrome stock for tremendously long periods of time. But I would say, in my estimation, that an extra day does not really make a lot of difference. Has anybody else had experience with the use of formates in connection with chrome tanning, and perhaps obtained more consistent results in coloring and fatliquoring?

MR. WENDELL MORRIS (Grand Haven, Michigan): I have noted that stock which has been tanned without the use of a masking agent may develop or show a condition of increased acidity the longer it stays on the floor after tannage, whereas a formate tannage usually becomes quite stable. In many so-called acid tannages after two or three days on the floor the condition of acidity in the stock increases as shown by a drop in pH value, and there appears to be some degree of reversal of tannage; whereas with a system of masked tannage the degree of tannage is more usually maintained without change by hydrolysis, indicating stability.

When stock out of a relatively acid tannage stands during vacation periods or such other lengthy periods of time, corrective adjustments may have to be made in the following processes. This is less likely to be necessary where a masking agent has been used in the tannage.

CHAIRMAN LOTZ: I would like to make one comment: Public relations and personnel men who keep negotiating away more and more holidays certainly do not do us tanners any particular amount of good. As we approach more and more these 9-day union-contractual paid holidays we are experiencing more problems from a strictly tanning standpoint.

MR. JEAN ROSEN (Blanchard Bros. and Lane): It has just been within the last few years that consideration has been given to the use of chrome tanning materials in upholstery leathers. As you probably know, upholstery leather is used mainly in automobiles and for furniture.

Up to two or three years ago all upholstery leather was produced strictly by vegetable tannage. In the last two years the automobile manufacturers have started to demand more and more light-colored leather for upholstery—

pure white and light pastel shades having been demanded from us in larger and larger quantities.

Apart from that, severe specifications have been set for us. The leather has to be completely stable to light, that is, completely lightfast. Samples of our finished hides have been put in a fadeometer and exposed for 120 hours. This is done all the time. The leather is exposed to ultraviolet rays under extremely high temperature and humidity conditions. Parallel to this, samples are exposed to the sun in Florida under extreme climatic conditions. After 120 hours the color of the samples has to be exactly the same as it was before it was exposed. This was quite difficult to accomplish by using vegetable tanning materials. No matter what type of vegetable tanning material was used—whether the pyragallol type or the catechol type—the leather used to change color when exposed to light.

Our company was among the first to give consideration to incorporating chrome tanning salts in our leathers. We do it as a retanning operation. After our leather has been split out of tan, it has been retanned with a certain basic chrome sulfate solution.

What we achieved was this: First, chrome salts are very lightfast. By adding them on top of a vegetable-tanned piece of leather, they precipitated uncombined vegetable tanning materials and, due to the difference in charge—as we know the basic chrome sulfate solution has a cationic charge and a vegetable-tanned piece of leather is anionic—the combination of these two materials fixed the grain and produced a piece of leather which, when exposed to sun or the fadeometer, did not change in appearance at all.

We had an additional advantage by using chrome salts. Our leather is usually embossed. Different patterns are set on upholstery leather. We use quite high temperatures in the embossing operation, and high pressure. A strictly vegetable-tanned piece of leather when exposed to this operation usually stiffened up considerably; however, when chrome was present, the leather finished up much softer than before, which is an advantage.

Within the past year and a half, I believe, the idea of splitting hides in lime has become more and more popular with our group. Here the opportunity presented itself to produce a piece of leather tanned with chrome. We all know of one company which uses chrome tannage as the basic tannage and follows up with vegetable retannage.

In our opinion this system has severe drawbacks. The discoloration by topping the chrome tannage with vegetable tanning materials is going to be a problem. We found also that by using vegetable tanning material on top of chrome, the tensile and stitch-tear strengths, which are very important in our case, decreased considerably.

We have tried consistently, and we are still trying, to produce a straight chrome-tanned piece of upholstery leather. So far I am sorry to say that we have not produced the results we want. The main reason is that stretch is one

of our worst enemies. You can imagine what would happen to a seat in an automobile, or to a chair or sofa covered with leather, if the amount of stretch is too great. The seat would go out of shape in no time at all. And in the case of extreme stretch, it would cause the finish to crack wide open.

I wonder if anybody here in the audience could suggest how to overcome the problem of stretch in a straight chrome-tanned upholstery leather. Mr. Morris is here, and he has done considerable work in this field. Could you throw some light on this subject?

MR. MORRIS: I am in accord with your opinion that the use of chrome in making upholstery leather is very definitely advantageous. However, I do not know of any way that you can make the straight chrome tannage as soft over the whole hide area as is desired presently for automotive upholstery and not have stretchy leather after the leather has been in use for a while. It is somewhat the nature of chrome leather, particularly when a soft leather is made with a considerable amount of fat liquor, that it becomes stretchy.

As to the use of extracts in retanning after a chrome pretannage, I am not entirely convinced that the lightfastness and crack test need necessarily be inferior. I think it depends on the type of extract, the amount of extract, and the basicity; and that it can be controlled through such factors as basicity in the pretannage. The excess nontannins in the chrome tannage can be washed out and colorfastness improved by after-treatment.

I believe the presence of chrome in the leather has a definite advantage also in the fixation of fat liquors where you want them more easily than in a straight vegetable tannage.

MR. ROSEN: We tried to vary the chrome tannage and the vegetable retannage. The more the leather was tanned with vegetable retannage, the worse the tensile and stitch-tear strength. But if we do not tan heavily, our leather is too flat. Our type of leather required softness, but at the same time no stretch. We could not find any way without using a heavy vegetable retan to get the round, full feel. But as I said, the tensile strength is then much below the requirements.

MR. MORRIS: As to the matter of loss of tensile strength by vegetable retannage—in the retanning of chrome-tanned stock with vegetable extracts for shoe leathers it is also desirable to manipulate the tannage so as to obtain a full, round feel with softness or mellow character without undue loss of tensile strength. And the process can be adjusted also in pretannage and after-treatment for upholstery leathers so as to secure good strength.

CHAIRMAN LOTZ: Mr. Hirsch, I wonder if, in any of your work in the mechanical leathers, you have come up with anything that would be an answer. I know you work to certain stretch specifications. Is there anything in the

work on mechanical leather that would lead you to believe that you could take a combination-tanned piece of leather and get a stretch as low as 10%?

MR. ARTHUR HIRSCH (Albert Trostel & Sons Co.): No, I do not think that we could get the stretch below 10% with the regular chrome retan leather.

CHAIRMAN LOTZ: Could you give us the minimum amount of stretch that you think could be obtained with that type of tannage?

MR. HIRSCH: I would estimate you would end up with a minimum stretch of 25 or 30%, with the way we tan our leather, our mechanical leather.

CHAIRMAN LOTZ: Are there any other comments on stretch in combination- or straight chrome-tanned leathers?

MR. ROBERT G. WELDON (Seton Leather Company): We started talking upholstery leathers, and I am in shoe leather. Upholstery leather is a side line with me. I cannot give you the reasons why, but if you set out to tan a piece of upholstery leather with a straight forward chrome tannage, I think you would come up with as good a piece of leather as you would ever want to see. It has been our experience that it wears pretty well and does not stretch.

MR. MORRIS: When you are speaking of upholstery leather, are you speaking particularly of furniture upholstery, or automotive, or either one?

MR. WELDON: Either one.

MR. MORRIS: I think that there is a little different problem with automotive leather in that respect than there is in furniture leather generally. Am I right, Mr. Rosen?

MR. ROSEN: Yes. And when you said that the leather does not stretch, could you give me the percentage of stretch which you have in your leather, Mr. Weldon? When you say it does not stretch—maybe visibly it does not. But if it has 20% of stretch, you would not notice it unless it was used severely and for a long period of time. Even 20% would not be too noticeable right away, but according to the specifications it is already away above the tolerance.

MR. WELDON: If I don't notice it and you didn't notice it, maybe the specifications were wrong.

CHAIRMAN LOTZ: Have you ever tried to argue with General Motors? That is essentially the problem that most of these upholstery tanners are faced with today—the specifications imposed upon them by the automotive industry. The

specifications themselves are almost impossible, and yet these tanners must work within a specification framework and deliver leather.

MR. ROSEN: Did you count how many times you bounced on the seat? And how long?

MR. WELDON: No.

MR. HIRSCH: The stretch of leather has a lot to do with how you dry leather, too. I would say if I had the task of making leather so that it had 10% stretch, or little stretch, or less stretch than we have now, I would dry it differently. You would have to let it cool and dry slowly, and then you would get most of the stretch out.

MR. MORRIS: As to the factor of stretch—in mechanical leather you have a solid, thick piece of leather, and by comparison with upholstery leather tanners, you would use less fat liquor. The upholstery leather is a lightweight leather and with possibly more fat liquor than you have in the heavy mechanical leathers.

MR. ROSEN: May I add to that? The upholstery leather, when finished, has to be within 3 to 3½ ounces and has to be of a soft, glovy-type nature.

MR. BERNARD: I would like to suggest that the stretch has something to do with the tanning, but there are some other factors, I believe, that determine the stretch. It is well to consider first that the setting out should be done very well. If the leather is toggled or pasted, this can start to take the stretch out. However, in finishing, if the leather is wet and then dried quickly, there is a very large shrinkage in the leather which, in stretch testing, must come back.

We have a very light, colored, full-chrome garment leather made from goatskin, and it must be soft. In some cases we have to retoggle that leather after we apply a finish, because with the amount of moisture that is in the leather it shrinks. It also becomes too stretchy, but it won't lay out if you have to do any other operations on it. So that it is the mechanical as much as the chemical treatment which prevents too much stretch in the leather. Too much heat in the finishing also will shrink the leather, and that has to come back again.

CHAIRMAN LOTZ: We don't want to get too far afield from chrome tanning. We can trace the matter of stretch to a number of other places in the tannery. I think the point has been well made that stretch is affected by other parts of the process.

One subject which we have not finished is the methods of chrome tanning. A great many of us use drums, but there is the continued use of paddles. We know of tanneries that are using both paddle tannages and drum tannages with

some different results. I wonder if anyone would like to comment on paddle tannages versus drum tannages, from experience.

MR. LAUREN E. MEYERS (Pfister and Vogel Tanning Company): I am going to turn that over to Mr. Fleisch. We have had quite a little experience with it.

MR. FLEISCH: For the past 40 to 50 years we have been paddle tanning. Then we decided we needed to go to drum tannages because of various conditions in the tannery. We started out by making a brief review of what we had done in paddle tannage. We reduce our own liquors. In our paddle tannage we had a take-up efficiency of 50 or 55%, which meant that we were throwing 45 or 50% of our chrome down the sewer. Under war conditions we had to do something about that. After the war we continued along those lines because of the high price of chrome and everything else.

Under the paddle tanning system, we started our pickle with 40% of our chrome in with the pickle, contrary to what most people are doing, I believe. When we went to drum tannage, we decided that we wanted to make the same leather we had been making under the paddle tan conditions. We started out using 40% of our chrome right in with the pickle, a very short pickle by usual standards. Yet, when we were through with our experimental work (well, we never will be through, but we are doing 100% drum tanning today), we made a piece of leather that was the equal of what we had made in the paddle. As a matter of fact, I would say it was tighter leather and possibly a little more mellow.

There is one thing we ran into, and we have not succeeded in overcoming it completely as yet: With increased forced feeding of the animals and with more and more kidney grease in the skins, for some reason the drum tannage seemed to bring the greases more to the surface. I don't know whether it was mechanical action or the fact that it was a shorter, more concentrated, process.

One other thing we did was to change the basicity of our chrome liquor. We raised the basicity of our chrome liquor from 37 to 43%, and we made a tighter piece of leather while going up in basicity. While this could compensate for the amount of acid we used, we found we got a slightly darker piece of leather, and we still have that problem of making the leather lighter, which of course the syntan people are happy to hear.

Other than that, we saved ourselves a lot of time and labor and saved ourselves a lot of space in the tannery.

MR. MEYERS: I would like to add that the drum process has also made a more uniform piece of leather.

CHAIRMAN LOTZ: One phase of chrome tanning that is of interest to some of us is on the actual construction of the equipment itself. Since you have put in

a relatively new drum installation, could we hear what your problems have been in that installation?

MR. MEYERS: These drums are wooden drums. They are 7 feet across and 8½ feet in diameter. We were able to put a lot more stock in such drums than we did before. At present we are putting in 7,000 pounds of white weight. I understand that is small because some of the people who have visited us and have seen what we did are now making drums that are 10 feet by 10 feet. Mr. Fleisch wanted larger equipment, but some of the rest of us were a little reluctant to go quite so far and settled on 7,000 pounds.

These drums all have direct drives with roller chain instead of belts. The V-belts are quieter, but the roller chain is certainly an improvement as far as we are concerned, and we like it very much.

In order to run these it takes a 25 h.p. motor which operates through a speed reducer to the chain. We use a Falk speed reducer, a Twin Disc fluid clutch, and a Cutler and Hammer magnetic brake. It really makes a wonderful setup that is easy to control. We can run the drums in either direction. Mr. Fleisch has reasons for that, and it has worked out very satisfactorily. If there are any questions, just ask us.

MR. BERNARD: Pegs, or shelves?

MR. MEYERS: Pegs.

MR. BERNARD: What is the speed?

MR. MEYERS: 18 rpm for the speed. As to the door, that is a different situation. We have a large door, 40" by 40". It is not a heavy door because it is plastic. It is something which an engineer worked out for us. We do not change doors; I mean, we do not lift the doors out of the drums. They ride on a track on the inside of the drum, and when we wish to wash, it is merely a matter of a few minutes to release the solid door and move the perforated plastic door into position. Incidentally, a patent for this type of door has been applied for.

The liquor is fed through a box. We happen to have it on a mezzanine, and we have a wooden box into which we put our salt brine, acid, and chrome liquor. These are fed by gravity into the drum.

The fast drainage is through the perforated wash door. We have on the interior of the drum a very simple device to measure the volume of float. It is an ordinary wooden gauge on the inside marked for the various floats which are needed, and it is easily observable even through the perforations in the wash door.

The instrumentation, so far, has not been perfected. We have experimented with a type of instrument with which we are not satisfied, and therefore we

would just as soon not comment upon it until we do have something that is more worthwhile.

The loading is done by means of an overhead crane. The unhaired stock is loaded into strong boxes reinforced with stainless steel, and as they move from the unhairing machine, they pass the scale where they are weighed. The crane lifts the boxes to the mezzanine and to the drum, and a simple tripping device dumps 3,500 pounds of stock into the drum at a time. Two loadings do it.

We have not used the large drums for coloring yet. However, we do have one large plastic drum of the same size—just about the same size—in which we will probably do some coloring experiments once we do not need it any longer for tanning.

MR. BERNARD: What type of bearings do you have?

MR. MEYERS: From the Stehling Manufacturing Company, and if you would mention a couple of kinds——

MR. BERNARD: Roller? Plain babbit?

MR. MEYERS: They are babbited bearings. They are not roller bearings. Of course, there is a stuffing box to prevent leakage.

MR. LAMMERT: Do you bate, pickle, and tan in one operation?

MR. MEYERS: It would be old-fashioned if we did not.

MR. LAMMERT: I have found, when washing in a drum of this size, that we need an enormous flow of water, obtained either by high pressure or larger pipes. I have found that it was a good idea to have the feed pipes going in from both sides of the drum in order to expedite the washing operation. It is very possible, when you feed only from one side, that it will take a long time for the wash water to get over to the other side. That is one question.

A last question I have is: Do you have the drum set rather high? Can you dump the entire load into a box?

MR. BERNARD: And I would like to ask Mr. Meyers what he does about the grease in the tan. Do you have any way to correct that in the tan?

MR. MEYERS: I will let Mr. Fleisch take that. I will answer Mr. Lammert's question and sit down. Because we load from a mezzanine level we have about 5½ feet below the drum, and we can dump the entire load into what we call a tanning boat. This boat is not perfected yet to our complete satisfaction, but it is working out quite satisfactorily at the moment. We have an incline under-

neath the drums so that once the boat is loaded—naturally with 7,000 pounds of white-weight stock it is pretty heavy—we can knock the blocks from under the wheels to let the boat move far enough away from the drum so that we can immediately start loading and washing again.

MR. MARTIN: Who makes these plastic drums?

MR. MEYERS: Carl Beetle, of Massachusetts. The eastern tanners know him very well. They make plastic doors, and they will make a plastic drum, too. But if you get one, be sure you have a door that you can get it through. We had to break out the concrete to get it in.

CHAIRMAN LOTZ: Now for the comments about the natural fat.

MR. FLEISCH: As I said previously, we have not completely solved the problem of natural fat. One of the things we do that we have found was essential and has helped us is to give a slight rinse in the tanning drum before we dump the tanned leather. Many people may consider this a waste of chrome. However, there is not too much chrome left in our tan liquor at that point. We have an efficiency of 90 to 92%, which I think is fairly good. Therefore we are not throwing too much down the sewer, and whatever chrome is in the leather should be fairly fixed at that time and should not wash out.

Then we have found that by letting our stock lie in our tanyard for an additional 24 hours, much of that natural grease that seems to break out and come to the surface—I am speaking purely of degree now, comparing drum tannage with paddle—is brought back to the condition obtained after the paddle tannage. We still have much kidney grease showing throughout our stock, and that we have not taken sufficient steps to overcome.

One other thing I would like to add to Mr. Meyers' remarks on the chain drive and stuffing box: One thing we insist upon is that we have a constant drum speed and that we do not lose liquor by leakage. Naturally, with 7,000 pounds of stock in the drum it is pretty well loaded, and we did not like the fact that we were losing about 20% of our chrome liquor. We put the stuffing boxes on, and so far they seem to work very satisfactorily. Our speed of 18 rpm is maintained within one revolution. In other words, 18 rpm plus or minus a half.

Then an additional comment to Mr. Lammert about water: We also find that we need a good flow of water. As a matter of fact, our water goes into that drum at the rate of 190 gallons per minute, and we use a 17-minute wash, all told, which amounts to a lot of water.

That, I think, we could lessen if the time comes when they increase the water rates (which is probable). In Milwaukee they are probably going to put a sewage tax on the amount of water going into sewage. That can be lessened by varying the amount of ammonium sulfate used for deliming and cutting

down the wash. At the present time it is a matter of economics. We feel that water is cheaper right now.

MR. BERNARD: Would anybody else like to comment on the grease in the tannage, as a part of the chrome tanning?

MR. GUY MOBERG (Northwestern Leather Company): We have just installed a drum also, and we have only experimented with it for three months. Mr. Meyers stated they have a chain drive on their system. We have a belt drive. It is a V-belt style, and we have it on both sides. I would like to ask about the door. We have a plastic door, but we find it is rather bulky and hard to handle. Can one man easily handle his door?

MR. MEYERS: Yes. It is on a rail inside the drum, and being plastic, it is very light and easy to manipuiate just by sliding it up on the inside of the drum. There is a little trick to manufacturing it. But it works out quite satisfactorily.

As to the chain drive versus belt, we have gone through the whole gamut of experience with flat belts, V-belts, and now finally chain drive. We have one experimental drum with which Mr. Fleisch has been experimenting for just about two years. He has lived with this, and he knows as well as I do about the problems that we had with flat belts and V-belts. This chain drive has been the answer.

MR. BENRUD: Would you be willing to comment on the temperature rise in a drum of this type?

MR. FLEISCH: Our material is fed in at 90°. When we come to our mixture of acid and chrome, we experience a rise of 95°. Our water and salt are put in at 90°, and our acid and chrome are added at 95°. We come out of tanning at 117°, plus or minus 3. In other words, 115° to 121° would be our spread. We would like to keep it a little closer, if possible. As yet we have not found why the rise varies as much as it does except for the stock. If we are running extremes, then we find our temperature does not go up as high as it does with full-sized heavyweight sides.

DR. THOMAS C. THORSTENSEN (Lowell Technological Institute): I would like to ask Mr. Fleisch a question. Here we have a case where a change was made from a paddle tannage to a mill tannage, and quite probably he has a very definite difference in the temperature of operation. I was wondering what his experience has been as to the effect of this higher temperature on the grain of the leather.

MR. FLEISCH: Not too great. In our paddle tannage we had our paddles covered and ended our tannage at 95°, so that we actually have not too much

of a temperature spread. As far as fixation of chrome is concerned, by stratographic analysis we find slightly more chrome in the grain and in the flesh than we had in the paddle tannage, but our chrome distribution curve is essentially the same. We have more chrome on the center of our stock than on the grain or flesh, and we tried to retain that particular curve on going into our drum tannage. You would say there must be more chrome because of the fact that the grain is somewhat darker than it is in the paddle tannage. But the difference is not enough to detect analytically. It is within the realm of experimental error. In comparing stratographic analyses of the paddle stock with the drum stock, they fall within the same range. If you compared one piece exactly with another you might be able to find a difference, but other than that, no.

MR. LAUDER: You stated that originally you had a waste of 45%, and then you remarked that finally you had 92% efficiency. I would like to ask what process changes you made to arrive at that 92% efficiency.

MR. FLEISCH: We cannot compare one with the other. One was a paddle tan. In the paddle we had 45% waste, and in the drum we have 8 to 10% waste. Other than that, we had very litle change. We regulated the amount of chrome we put into the drum to yield the amount of chrome we wanted in the leather, with very little of it being thrown down the sewer. We are getting that result in the drum where we could not in the paddle.

MR. J. HERBERT STUMPF (Chemtan Company): A considerable number of tanners in the Middle West use syntans in connection with the chrome tanning. One of the advantages is dispersion of the natural animal fat. That may be one of the solutions to Mr. Fleisch's problems.

MR. ROSEN: Has anybody in the audience tried to use emulsifiers together with his tannage, or sulfonated alcohol? I know grease is a problem to many of us, and I know some do use emulsifiers. Some use them in the bate and in the pickle, and some use them all through the tannage. Would anyone care to comment on that?

CHAIRMAN LOTZ: Mr. Retzsch, will you comment?

MR. CLINTON E. RETZSCH (Nopco Chemical Co.): We have seen instances where leather was filled with grease spots, particularly in the kidney area. By the use of 0.25% of nonionic degreasing agent in the last 30 minutes of the bating operation, this condition was completely eliminated, so much so that the men splitting the leather in the blue, not being told what had been done back in the beamhouse, immediately observed a definite difference when putting that leather through the splitting machine. Prior to the use of the degreasing

agent they were having considerable difficulty in splitting the stock. We had to set the rollers down to such a degree that the leather was difficult to handle, and they were getting nonuniform splitting. By the use of the emulsifier in the last 30 minutes of the bating operation, the stock went through the splitting machine without any difficulty. It meant a saving of time and a better piece of leather, and at the same time it eliminated the grease built up on the felts when they were wringing. That is our experience on the use of degreasing agents in the bating operation.

CHAIRMAN LOTZ: Mr. Stumpf, haven't you had somewhat the same experience with the addition of syntans as far as wringer felts and grease are concerned?

MR. STUMPF: Yes. One of the other properties produced by a syntan seems to be a more permeable cell structure in the leather. In other words, the water seems to be squeezed out of the leather more easily. Some tanners have reported that they can reduce the pressure on the wringers by as much as one-half and still get the same water content, and more uniform water content, in the leather after wringing. This has meant quite a considerable saving in the cost of felts.

MR. ERNEST H. STEIN (General Shoe Corporation): In our tannery we were having trouble with certain lots of feed-lot hides, and by the use of 0.1% of neutral syntan added with the chrome our wringing troubles and our felt troubles were pretty well solved. The skins shave better, and it has helped all the mechanical operations. We see no bad effect later on in the process. I have always been worried about using emulsifiers, and I would like to ask Mr. Retzsch how long the emulsifier stays with the leather.

MR. RETZSCH: I would like to answer Mr. Stein by saying I am sure that there are several tanners here in the room who are using the product, and I am certain that if they would just get up and comment, it would help considerably. This is a practical tanning symposium, and we are not trying to advocate any particular product of ours. I wish that some of the men who are using it would give an answer as to whether or not they are experiencing any difficulties later on from the use of that nonionic material.

MR. CHARLES T. CARES (John Flynn & Sons, Inc.): We make cowhide garment leather. We had a problem with grease, and it bothered our splitting considerably. We went to a nonionic emulsifier (it does not happen to be Mr. Retzsch's) and it works very well with us.

MR. OSCAR V. WEDERBRAND (Rohm & Haas Co.): The only thing I want to say is that we are selling to the tanners wetting agents which they are using

in various spots in the process. Some of them put them in the bate, some after the bate, some in the chrome tan, some as a wash after the chrome tan, and some people will add them to, or after, the fat liquor. There are tanners here who are using these materials. I am not at liberty to mention names, but I am sure that, as Mr. Retzsch said, they could add to this discussion at this point, if they care to.

CHAIRMAN LOTZ: I think a point has been missed here. Someone asked the question: Once you get the emulsifiers in, do you get rid of them in the future process?

MR. RETZSCH: I would like then to go a little further with it and suggest that since the material is nonionic in nature, once it has done its job of emulsifying the grease in bated stock, there is no reason in the world for it to have an affinity for that stock. Therefore it is readily washed out. The same is true in any case where it would be used in such a low concentration, as a washing agent. It will definitely wash out and not remain in the stock to give any difficulty later on, in any type of operation.

CHAIRMAN LOTZ: Mr. Wederbrand, is that your experience too?

MR. WEDERBRAND: The only difficulty that any of our customers have reported to us is when they have used it on top of fat liquor. Some customers have had difficulty in fatliquoring, and they have found that putting a nonionic, or sometimes an anionic, on top of the fat liquor will disperse their total grease a little bit better. They have reported difficulties there with excessive penetration of the finish and sometimes, if they go too far, with a too easy rewetting of the finished leather. The latter has been particularly true in suedes. That is all I can add on that.

As to Mr. Stumpf's mentioning of syntans, I can vouch that there are a lot of tanners who have reported exactly what Mr. Stumpf has said. As Mr. Stein mentioned, the addition of a syntan during the chrome tanning operation, either a neutral syntan after the chrome tan, or acid sytan with the tan, has definitely helped. I do not think it is grease removal or emulsification, but really grease dispersion more than anything else.

As far as the addition of the wetting agents or nonionics to the bate, or after the bate, we have run analyses on comparative packs (drum-bated stock). One drum received a nonionic with the bate. The other one received just the ordinary bate. We analyzed pickled skins from both of those packs, and we could find no difference in the grease content.

CHAIRMAN LOTZ: I would like to ask Mr. Stumpf a question. These people seem to indicate that these nonionics are eventually removed since they contain no reactive group which will bind to the skin. Syntans however are essentially

anionic, and there must be a combination with the skin that will show up in the processing. What is your thought on this?

MR. STUMPF: I think the syntan would become attached to the skin. However, the quantity of syntan that is used is so small as to have very little effect on the final properties of the leather. I believe the advantages are primarily mechanical during the processing.

CHAIRMAN LOTZ: Is there anyone else who has used syntans, or emulsifiers, who would like to comment on their connection with chrome tanning?

MR. FRANK EDMONDS (American Cyanamid Company): We have not had too much experience with the nonionics. But we do know of one tanner who is using them, and all I can really add is to confirm more or less what Mr. Retzsch and Mr. Wederbrand said about the products. In regard to the neutral type of syntan, I think from what Mr. Stumpf said that the amount used would make very little actual difference. Because it is a surface reactor, it should not create any problem later on, particularly where leather is being buffed. In fact, if there are any color problems arising from the dyestuffs that are subsequently used, the small amount of syntan would act as a leveling agent and improve rather than deteriorate the leather in any way.

MR. MARTIN: Some years back a Philadelphia goatskin tanner, after fleshing, washed his skins in a nonionic agent. This was previous to a two-bath tannage. It did an excellent job of cleansing the grain and cleaning the stock for the bating and pickling that followed.

CHAIRMAN LOTZ: One of the subjects that seems to be of some interest is the effect of the end temperature in tanning on the amount of chrome that is fixed. Some work of a technical nature has been published on this from time to time, but I am wondering if anybody has had practical experience on the amount of chrome fixed versus the temperature at the end of chrome tanning.

MR. WENDELL MORRIS: I think it is quite probably the general experience that increasing the temperature during tannage has quite an effect on the amount of chrome fixed and on several physical characteristics of the leather. Due to the particular conditions that may exist in any individual tannery we may have different tanners turning out drum tannage leather with final temperatures from 95° up to 120°, as reported by Mr. Fleisch. It has, in a general way, been my experience that, particularly above a temperature of 115°, you get quite a drawing effect—a rather accelerated drawing effect on the grain, a little tighter grain, and a drawn condition.

I think the temperature also has a little relation to the removal of the natural grease in the hide, that a tannage terminating at 115° is likely to remove more of the natural grease than at a temperature of 100° or under, and that a terminal

temperature over 100° will more particularly bring about stability of the stock in relation to the lag period between tannage and coloring.

MR. SALAMATOV: Last year at the discussion of chrome tannage I asked the same question on the floor, and it was answered by Leo Riese. He said at that time that they ran several packs of leather at an elevated temperature of 110°, and he gave figures for the fixations of the chrome.

I think it is readily understandable that higher temperature will promote hydrolysis and the promotion of hydrolysis will further accentuate the fixation of the chrome on the surface, and the amount of chrome retained by the skin will certainly be greater. But the question is whether or not this additional fixation of the chrome will improve the leather. It may be that the chrome has been precipitated in the grain and made it breakable or cracky, or it may be a gradual absorption which simply increased the absorption of the chrome in the fibers and made a fuller leather. This question has not been answered.

CHAIRMAN LOTZ: Are there any others here who have had experience with the effect of the end temperature on actual characteristics of the leather?

In our own experience we take most of our chrome tannages out at a temperature of between 105° and 110°. That goes back to the time when Mr. Morris set up our chrome process. We find that at elevated temperatures (over 120°) we get different grain characteristics which we do not particularly like.

If the leather comes out of tannage at too low a temperature, you do not set enough chrome or get enough benefit from your total chroming system.

I wish Dr. Stubbings were here to comment on this because he has done a considerable amount of work on end temperatures.

MR. ROBERT S. KATZ (Superior Tanning Co.): We have observed an interesting phenomenon, that in our regular tan we come out with a comparatively high temperature, in the neighborhood of 120°. We did run sample packs of a combination pickle-tan, a masked tan proposition, and our final temperatures came out as much as 20° lower, yet we fixed roughly the same amount of chrome with a very slightly higher final pH. This seemed to us rather unusual in the light of some of the previous work which has been done in this field.

CHAIRMAN LOTZ: We have gotten to the point where we have exhausted a great many of the factors of chrome tanning. We started out with a list of 20 side subjects here, some of which we have not gone into—things such as chrome tanning versus army specifications. But I am sure that some of you may have some questions you would like answered, which we have not introduced.

DR. H. B. MERRILL (B. D. Eisendrath Tanning Co.): Going back to the question of addition of wetting agents in bating, it has been reported recently,

from Czechoslovakia, that the addition of certain detergents has a very strong activating action on the enzyme used in bating. They ran into some trouble until they compensated for this action. How much there is in it, I do not know, but it is something that might be thought about.

MR. B. A. SCHILLER (Nopco Chemical Company): I was hoping someone would bring up a point that I personally noticed six or seven months ago in a sole leather tannery. We tried to use the degreasing agent where they were bating in a paddle, and we were not too successful because the hides sank to the bottom, so that we found we could not do the degreasing in that particular process. But what it did show was that the use of the degreasing agent did remove the grease and reduce the surface tension, which in turn opened up the hide. We then tried it after bating in the drum, and here it worked very well. Then when we came to the first day of bark tanning, we found that the grain took the color much more uniformly than the hides that had not been degreased. I think that, from a practical standpoint, that observation in itself indicates a very definite use for a degreasing agent.

DR. THOMAS THORSTENSEN: We have been talking rather extensively about the use of wetting agents and other materials for cutting down the grease. I think there is one point on the grease question in the chrome tannage that I would like to make, and I put it out for what it is worth.

You will find that the grease problem will vary considerably from one tannery to another, and this in cases where no wetting agents or dispersing materials may be used.

Now, in a given tannery, all other things being equal, we can refer back to Dr. Turley's diagram (Figure 1), and I think that the practical tanners here have all observed one fact, that if they are working more to the left, in the acid tannage range, they find that the grease is a bit more prevalent than if they work in the higher pH range. That is quite easily observed, and I think you have probably all observed it in your own production.

MR. BROWN: May I ask the panel a question: What is the purpose of chrome retannage? We do not use it.

CHAIRMAN LOTZ: It goes back to this diagram (Figure 1). You start out with a chrome tannage, and you are operating somewhere in this system on your basic chrome tannage; then by a method of retannage, including chrome—or it could be vegetable or something else—you try to change part of this pattern and shift it. That is the significance of chrome retannage. A tanner starts with a basic process and then wants to make a different kind of leather, and you use chrome retannage to shift this particular pattern. Does that give you part of your answer?

MR. BROWN: Yes and no. You mentioned that you can shift up, but you cannot shift back.

CHAIRMAN LOTZ: Yes, you can shift back partially. Again you have to remember that a tannage is an integrated thing. A good bating shifts you from a coarse and pronounced grain to a flatter grain. A good soaking may shift the pattern too. We do not have trouble with grease spots. We use a brine soak and flesh all the grease off in the beamhouse. Another part of the process can change the grain pattern too. But basically, if your tannage gives a medium grain, you cannot shift back to the flat grain of a high acid tannage (low pH), unless you use a miracle material. Suppliers are getting closer to them, I suppose, but it is very difficult to correct a high grain effect—the formate type of effect, I call it—as far as heavy side leather is concerned. If we have to make a smooth dress leather, we need to dilute this effect, and it is difficult to do. The only way to stay in the middle range is to change the chrome procedure and move down definitely on the acid side, and definitely without formates. And incidentally, as long as I am discussing this thing, one phase that we have not discussed which is of interest to me is the effect of chrome tannage on retannage. With the increasing use of vegetable retan materials, a combination of materials, and now the whole new concept of the use of resins for retannage materials, the effect of the primary tannage on the retannage becomes of considerable importance.

For example, the way you reduce your chrome and the amounts of cationic and anionic chrome in the chrome liquor determine your ability to pick up a retannage material.

Specifically, when we are using resins, the higher the anionic portion of the chrome, the greater is the ease in retanning with resins. That is one reason why in our tannery we reduce our chrome liquors with the acid added last. We get a higher percentage of anionic chrome in the chrome liquor. It gives us greater ease of handling vegetable retan materials and a greater ease in handling resins.

This is probably a controversial field, but most of our own theory and thinking came out of the work that Dr. Otto did—the very basic work that he did—on electrical charge mechanisms. We have not as yet really found an accurate tool for determining the amount of cationic and anionic constituents in the chrome liquor. But we are getting closer, and we have some rough ideas. We have not an absolute value, but we do have a comparative value, and we know that the type of reduction definitely gives a difference.

Is there anyone who has had experience in connection with the retannages and the effect of chrome reductions on retannages, who will not agree it is an interesting field? It is in the field of retannages that we create our types of leather; very little leather today, comparatively, is straight chrome-tanned. Possibly calf leather and lightweight dress kip are exceptions. But certainly in the side leather field, particularly in the United States, the whole field of

retannage has become almost more important than the tannage, and I know that no tannery can exist competitively in that field without a complete and thorough understanding of chrome tannage.

MR. MORRIS: I think oftentimes the determination whether to retan or not is based on a way of doing things traditionally in the tannery. It is a matter of balance of the process all the way from beamhouse to staking. You may be able to bring out the leather in one straight tannage with sufficient chrome to get the softness desired. Conditions of hard water, or neutralizing, and a high terminal pH of tannage, and any great degree of staking, will bring about the softness desired. And yet that tannery may not be able to chrome retan because they have softened the leather to such an extent that staking would spoil the character of break and such.

In tanneries where it is customary not to stake, or to give a very light staking, retannage may be of assistance. Therefore, I think that some tanners who question why to retan at all have a balance of their processes, from the beamhouse through the tannage, that brings about the characteristics that they desire, whereas another tannery may require the retannage because of a different balance of process.

MR. HAROLD R. MILLER, JR. (A. F. Gallun & Sons Corporation): One other factor which might influence your decision to retan, either chrome or vegetable, probably would be what you get out of a certain pack. In our case, with calf, LLL's are not exactly the most desirable thing to have going through the tannery. Often you can make them into LL's, or even LM's, by the proper retan.

MR. BROWN: Do you think chrome retan would be effective in increasing their weight?

MR. MILLER: We have found definite indications that this is so. It depends on the type of retan that you use. We have been experimenting recently with a two-bath retan. Our normal tannage is a one-bath pickle and tan. Then, after splitting and shaving, or in the case of these light skins, just shaving alone, we find that if we take the LLL's and treat them with bichromate for one to two hours and then reduce with sodium bisulfite, we get a tremendous increase in thickness with a resultant mellowing effect on the leather.

DR. MERRILL: I can confirm what Dr. Harold Miller has said, except that we have not had the luck to transform LLL's into LM's, but we did get a definite increase in substance along with a mellowing effect. Incidentally, with the two-bath tan such as Harold Miller has described, we got a very uniform distribution of the chrome throughout the whole thickness of the skin. At one time, for certain types of leather, we gave a one-bath retan, after splitting

and shaving. We found that nearly all the additional chrome taken up in that treatment was in the flesh and grain layers.

MR. MARTIN: I would like to ask both of you a question: Where do you get the LLL's—out of four-to-five's or three-to-four's, or what?

MR. MILLER: Unfortunately they can come out of nine-to-twelve's, depending on where they are from. That is a facetious remark, but I would say anywhere from five's to seven's, on down, especially in the Holstein spready-type skins.

MR. MARTIN: We have not run into the LLL's. That is why I ask.

MR. SALAMATOV: Was that retan on top of the chrome tan?

MR. MILLER: Yes. It was after shaving. By LLL's I mean 3- to 3½-ounce double leather, in the blue.

MR. SALAMATOV: I might add my comment. Once we bought a very large pack of skins from Italy, and they were all below the required weight. They were retanned after shaving with the one-bath chrome and gained one quarter to one-half of an ounce.

MR. ROSEN: Mr. Miller, did you notice a decrease in yield?

MR. MILLER: We do not have enough data, yet, to give a really definite answer on that. I would suspect that there would be a slight decrease in yield, but it should be more than overshadowed by the fact that you have a plumper leather.

CHAIRMAN LOTZ: Does anybody have questions or thoughts on the rate of addition of the chrome liquors to the tan mills? Does everybody add it in one feed? In some instances I know, some American tanners, as well as European tanners, put a low basicity liquor in first and follow later with a higher basicity liquor. But has anybody experience on the rate of addition of chrome to the mill? Do you feed it at once or in two feeds?

MR. STEIN: I think that the addition of all the chrome at one time would give you the better result because you add all the available acid to the leather. That is especially true in a short pickle, one-bath tannage. If you add small increments, you have a very high basicity to start with. By feeding all at once, you start with a low basicity in the over-all system.

MR. MILLER: I would like to take issue with that. Mr. Stein is making side leather, and we are making calf. Our experience has been that if we add our

chrome liquor all in one feed, we will have dark spots in the bellies and flanks and along the rib lines. We call them chrome spots. They look like chrome spots—dark green, especially after neutralization. We find we can minimize them by slowing down the rate of addition of our chrome, either on a pickle-and-tan or a separate pickle process, by adding our chrome in three to four feeds at 20-minute to half-hour intervals.

MR. MARTIN: I think you are absolutely right. Whether you start with a pickled stock or pickle and then continue straight through the tannage, you are raising your over-all basicity slowly as you add the chrome liquor, and I think you get a smoother grain and less chance of chrome spots. Any neutralization you do after that should be done in the same manner and not by adding a large amount of neutralizing agent at any time—for calf.

MR. BENRUD: There is one point that has not been covered at all, and that is the concentration of salt in the initial tan. I know there are some who think that it is important to have that very exact, whereas others will use quite large quantities of salt and without measuring it too accurately. Is there anybody who would like to comment on salt concentration?

MR. MORRIS: I do not know whether anybody would comment on how critical concentration would be in degrees. But if an amount equivalent to 5% of salt is sufficient, generally speaking, on side leather at least, why use 10%? I think it might be said that increasing the amount of salt makes for a softer leather, so that for a firm type of shoe leather it might be preferable to use a minimum amount of salt, whereas for a soft glove or garment leather considerably larger amounts of salt might be used for the effects of the salt on softness or stretchiness of the leather.

CHAIRMAN LOTZ: Gentlemen, I think we have done rather well this morning. I do want to summarize what we have done. Essentially we have taken up as many of the aspects of chrome tanning as we possibly could. I think we have pinpointed a lot of problems that we, as tanners, have to deal with.

I heard a very fine suggestion yesterday, and that is that the material of the last three symposiums and this one today be picked apart and a treatise written as a guide for future Tanners' Council programs.

In the past a gulf has existed between the practical tanning man and the chemist. This gulf is narrowing because of group discussions like this and our willingness as tanners to stand up and talk about our problems.

I think a greater understanding is developing because of symposiums like this. I think the theoretical men are beginning to get hold of some of the problems we have and which we consider most important today. And I think from this sort of program we eventually will move the industry along to a

point where it will be a lot healthier than it was ten years ago, and perhaps than it is now.

I want to thank all of you for your cooperation. I think it has been most gratifying that 100 different men from 100 different places in the United States and Canada are perfectly willing to get up and speak of their problems and also of their experiences.

I am sure this program will be continued next year at Lake Placid, at which time a new committee will probably go into another phase of tannery operations.

MR. MILLER: At this time I think it is proper for us to express our thanks to our panel and especially to our two last-minute fill-in members, particularly Charles Martin and Bob Lotz, who had to step in and fill the shoes of Frank Zeissig and Chet Ross, who unfortunately could not be here.

Also, we ought to express our thanks to the four Production Clubs—Wisconsin, Delaware Valley, New England, and the Canadian Club.

CHAIRMAN LOTZ: Gentlemen, our meeting stands adjourned.